Supporting Information of

Electronic structure study of singlet-fission in tetracene derivatives

David Casanova

IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Euskadi, Spain, and
Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), Donostia, Euskadi, Spain

Contents

Table S1. Experimental vibrational progression (Δν) and B3LYP/6-31G(d) computed symmetric CC stretching bond frequencies in solution (ν_{SYM}) in the 1200-1500 cm^{-1} region of tetracene and DPT in chloroform and rubrene in toluene. All values are in cm^{-1}.

	Tc	DPT	Rub
ν_{SYM}	1236	1406	1251
	1428	1428	1327
	1442	1433	1350
	1495	1491	1372
			1480
Δν (exp)	1402[1]	1398[1]	1300[2]

(1) Roberts, S. T.; McAnally, R. E.; Mastron, J. N.; Webber, D. H.; Whited, M. T.; Brutchey, R. L.; Thompson, M. E.; Bradforth, S. E. *J. Am. Chem. Soc.* **2012**, *134*, 6388.

(2) Petrenko, T.; Krylova, O.; Neese, F.; Sokolowski, M. *New J. Phys.* **2009**, *11*, 015001.

Table S2. Computed vertical absorption and emission and adiabatic excitation energies and experimental absorption and emission maxima and adiabatic for tetracene and DPT in chloroform and rubrene in toluene solution.

	ΔE_{abs}	ΔE_{em}	$\Delta E_{0\text{-}0}$
Tc			
B3LYP	2.74	2.50	2.62
ωPBE	3.09	2.84	2.96
ωB97X–D	3.20	2.91	3.10
experiment	2.61	2.59	2.60
DPT			
B3LYP	2.66	2.37	2.52
ωPBE	3.00	2.68	2.83
ωB97X–D	3.10	2.76	2.99
experiment	2.51	2.47	2.49
Rub-*flat*			
B3LYP	2.54	2.27	2.41
ωPBE	2.85	2.56	2.70
ωB97X–D	2.95	2.62	2.85
Rub-*twist*			
B3LYP	2.39	2.09	2.24
ωPBE	2.67	2.33	2.49
ωB97X–D	2.79	2.40	2.65
experiment	2.36	2.23	2.29

Table S3. Excitation energies (in eV) to the lowest excited singlet of tetracene, DPT and rubrene clusters as a function of the cluster size (number of molecules) as in Figure S1. All values computed with the ωB97X-D functional and the SBKJC effective core potential and basis set.

n	Tc	DPT	Rub
1	3.197	3.065	2.998
3	3.063	2.909	2.899
5	3.029	2.902	2.865
7	2.986	2.890	2.854
9	3.015	2.881	2.851
11	2.995	2.872	2.847
13	2.984	2.854	2.841

Figure S1. Molecular cluster models of tetracene (Tc-*n*), DPT (DPT-*n*) and rubrene (Rub-*n*) in Table S3.

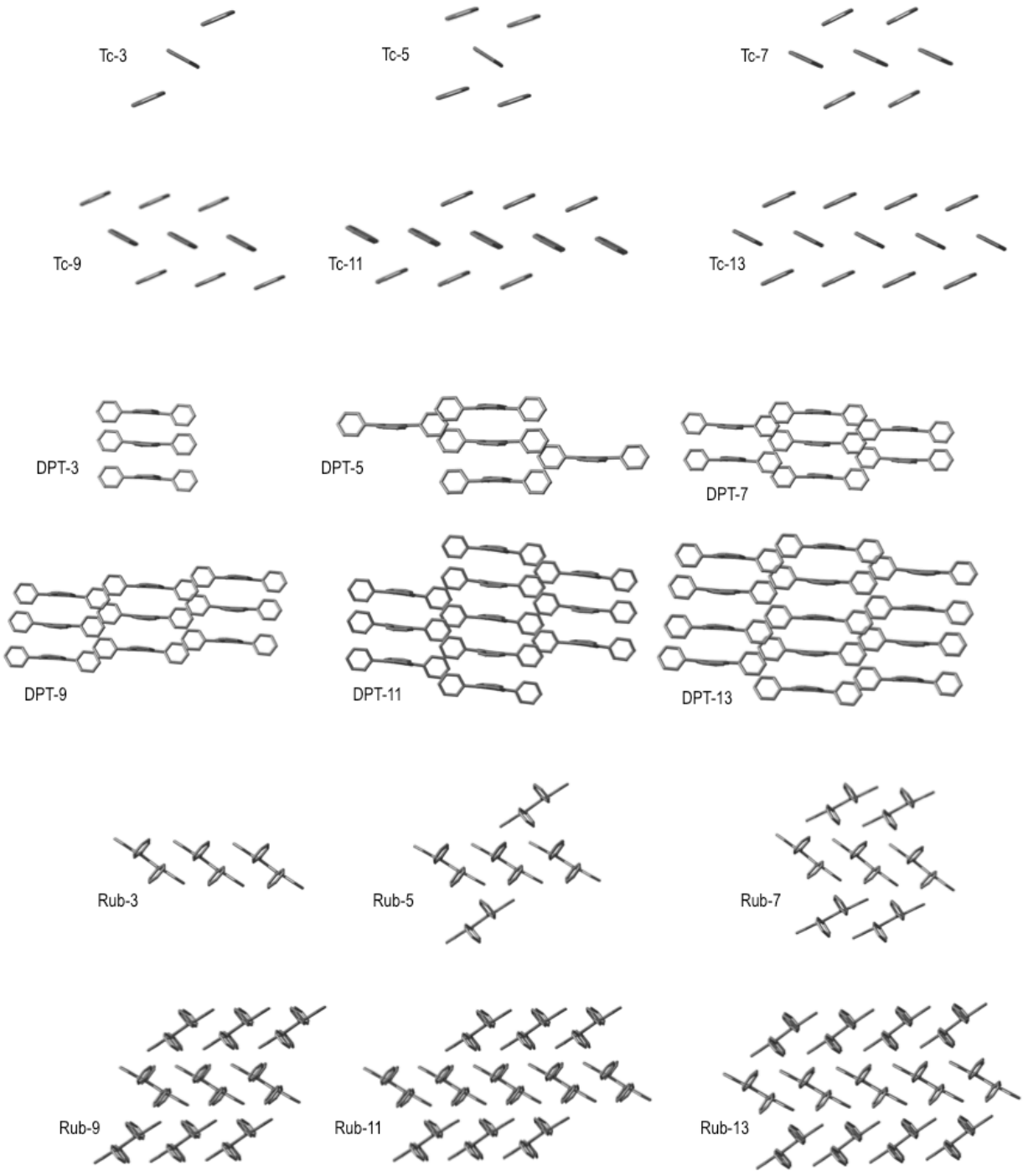

Figure S2. Nomenclature for the neutral and ionic monomer states.

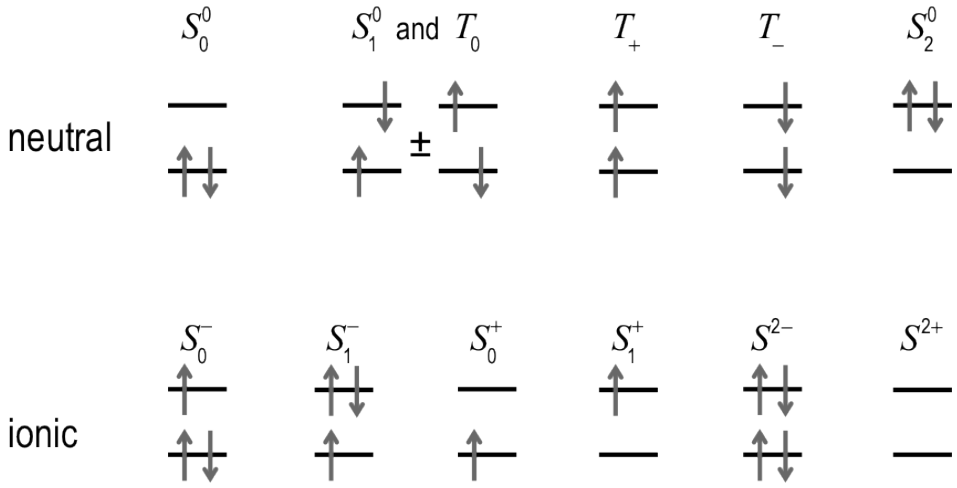

Figure S3. Spin adapted diabatic singlet states as the combination of monomer states. Column index refers to the degree of electronic promotion with respect to the full occupation of monomers' HOMOs.

0	**1**	**2**	**3**	**4**
$\|0\rangle = \|S_0^0 S_0^0\rangle$	$\|1\rangle = \|S_1^0 S_0^0\rangle$	$\|5\rangle = \|TT\rangle$	$\|15\rangle = \|S_1^0 S_2^0\rangle$	$\|19\rangle = \|S_2^0 S_2^0\rangle$
	$\|2\rangle = \|S_0^0 S_1^0\rangle$	$\|6\rangle = \|S_1^0 S_1^0\rangle$	$\|16\rangle = \|S_2^0 S_1^0\rangle$	
	$\|3\rangle = \|S_0^- S_0^+\rangle$	$\|7\rangle = \|S_0^0 S_0^2\rangle$	$\|17\rangle = \|S_1^- S_1^+\rangle$	
	$\|4\rangle = \|S_0^+ S_0^-\rangle$	$\|8\rangle = \|S_0^2 S_0^0\rangle$	$\|18\rangle = \|S_1^+ S_1^-\rangle$	
		$\|9\rangle = \|S_1^- S_0^+\rangle$		
		$\|10\rangle = \|S_0^+ S_1^-\rangle$		
		$\|11\rangle = \|S_0^- S_1^+\rangle$		
		$\|12\rangle = \|S_1^+ S_0^-\rangle$		
		$\|13\rangle = \|S^{2-} S^{2+}\rangle$		
		$\|14\rangle = \|S^{2+} S^{2-}\rangle$		

Note $|TT\rangle = \frac{1}{\sqrt{3}}\left[|T_0 T_0\rangle + |T_+ T_-\rangle + |T_- T_+\rangle\right]$.